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(74) Agents: SHERMAN, Lorraine, R. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(54) Title: ENERGY-CURABLE CYANATE/ETHYLENICALLY UNSATURATED COMPOSITIONS	
(57) Abstract			
<p>A composition of matter includes a polymerizable mixture comprising 1 to 99 weight percent of a first monomer and an initiator therefor, the first monomer being one of 1) at least one free-radically polymerizable monomer or 2) at least one cyanate ester monomer, and 99 to 1 weight percent of a second monomer and an initiator therefor, the second monomer being the member of 1) or 2) that is not selected as the first monomer, wherein the curative for the cyanate ester is a transition metal-containing organometallic compound curing agent and the curative for the free-radically polymerizable monomer is a free-radical generating curing agent or a transition metal-containing organometallic compound. The polymeric mixtures are useful, for example, in applications requiring high performance, such as high temperature performance; in composites, particularly structural composites; structural adhesives; vibration damping materials; electronic applications such as printed wiring boards, semiconductor encapsulants and electronic adhesives; photoresists; injection molding and preangs; protective coatings; tough self-supporting films; and high performance binders. In addition, a curable composition including (1) an ethylenically unsaturated monomer or (2) an ethylenically unsaturated monomer and a cyanate ester monomer, and certain organometallic neutral compounds is useful in the graphic arts.</p>			

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ENERGY-CURABLE CYANATE/ETHYLENICALLY
UNSATURATED COMPOSITIONS

Field of the Invention

This invention relates to polymeric mixtures and to precursors therefor and to a process for providing durable polymeric mixtures comprising polymerized ethylenically unsaturated monomers in combination with polycyanurates. In yet another aspect, articles comprising the compositions of the invention are disclosed. The polymeric mixtures are useful, for example, in applications requiring high performance, such as high temperature performance; in composites, particularly structural composites, structural adhesives; vibration damping materials; electronic applications such as printed wiring boards, semiconductor encapsulants and electronic adhesives; photoresists; injection molding and prepgs; protective coatings; tough self-supporting films; and high performance binders.

Background of the Invention

Industry is constantly searching for lighter, stronger, and more resistant materials to be used in place of the materials used today. Cyanate ester resins are known for their thermal stability, chemical inertness, solvent resistance, and electrical properties. Thus, more and more uses are being found which demand high performance materials, such as structural composites, printed wiring boards, semiconductor encapsulants, structural adhesives, injection molding and prepgs, and high performance binders. The high performance characteristics of cyanate ester resins are offset by their brittleness. To expand their utility, several strategies have been pursued to toughen these materials.

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Patents dealing with curable compositions comprising cyanate ester monomers and ethylenically unsaturated monomers include, for example, U.S. Patent Nos. 4,600,760, 4,116,946, and 4,383,903. Catalysts 5 used for cyanate cure are metal salts, such as zinc octoate, cobalt naphthanate, or certain amines.

Cyanate ester resins are formed from polyfunctional cyanate monomers. The use of an organometallic compound as thermal and/or 10 photocatalyst for the cure of a cyanate ester resin has been described in U.S. Patent No. 5,215,860.

The use of photoreactive organometallic transition metal carbonyl complexes in conjunction with organic compounds, such as organochalo compounds 15 (H. M. Wagner and M. D. Purbrick, *J. Photographic Sci.* 1981, 29, 230) and electron accepting olefins (C. H. Bamford and S. U. Mullik, *J. Chem. Soc. Faraday I* 1976, 72, 368), in free radical curing is known. For example, benzenechromium tricarbonyl with CCl_4 , has 20 been used to photopolymerize methyl methacrylate (C. H. Bamford and K. G. Al-Lamee, *J. Chem. Soc. Faraday I* 1984, 80, 2175) and styrene (C. H. Bamford and K. G. Al-Lamee, *J. Chem. Soc. Faraday I* 1984, 80, 2187); in both cases, the active initiating species has been 25 shown to be the CCl_3 radical and little or no curing occurs in the absence of CCl_4 .

Gatechair et al. (U. S. Patent No. 4,707,432) has shown the combination of certain cationic organometallic complexes, such as ferrocenium salts, 30 with α -cleavage photoinitiators, such as acetophenone, to be useful photoinitiator systems for free radical polymerizations. DeVoe and Palazzotto (EPO Publication No. 0 344 911 A2) have further shown that certain cationic organometallic complexes by 35 themselves are useful photoinitiators for acrylic polymerizations.

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Cyanate ester resins have been proposed for use in vibration damping. U.S. Patent No. 4,223,073 describes the use of polycyanurates in "high temperature damping" composites. These are single component systems in that cyanate ester groups are the only polymerizable groups present; thus, little control is possible over morphologies of the cured resin. Further, the "high temperature damping" appears to refer to temperatures of around 100°C.

10 Japanese Patent Applications 4,202,316, 4,202,353 and 4,202,354 all describe vibration damping materials comprising preformed saturated polyesters and cyanate ester monomers.

U.S. Patent No. 3,833,404 discloses a viscoelastic layer for use in a damping means for a vibratory part, the layer being an interpenetrating polymeric network (IPN). The IPN is prepared sequentially, wherein the first component is cured in the absence of the second component which is then added by swelling or combining the two components as latexes.

Electronic adhesives based on cyanate ester compositions cured with organometallic catalysts have been described in U.S. Patent Number 5,143,785.

25 Cyanate esters are combined with preformed thermoplastic polymers, conductive particles, catalysts and coupling agents in a solvent such as tetrahydrofuran and preferably coated on a release liner to provide an adhesive film.

30

Summary of the Invention

The present invention provides a composition of matter comprising a curable mixture comprising 1 to 99 weight percent of a first monomer and an initiator therefor, the first monomer being one of 1) at least one ethylenically unsaturated monomer or 2) at least

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one cyanate ester monomer, and 99 to 1 weight percent of a second monomer and an initiator therefor, the second monomer being the member of 1) or 2) that is not selected as the first monomer, wherein the
5 curative for the cyanate ester monomer is a transition metal-containing organometallic compound and the curative for the ethylenically unsaturated monomer is a free radical generating curing agent or a transition metal-containing organometallic compound, the
10 composition being capable of providing an interpenetrating network comprising a semi-phase separated morphology. The unique combination of curatives surprisingly provides the cured mixture with this desirable morphology. The use of two or more
15 independently partially polymerized ethylenically unsaturated monomers is useful in providing the desired morphology.

The curing agents for both monomers independently may be thermally or photochemically activated.

20 In another aspect, processing methods for controlling the sequence of cure of the components and thereby controlling the morphology, and thus the properties, of the cured composition are provided. The polymer precursors may be cured by a sequential or
25 simultaneous curing process.

Coated articles can also be prepared according to the invention by coating an energy polymerizable mixture as described onto at least one surface of a substrate, then applying energy (after evaporation of
30 any solvent) to the article to cause polymerization of the coating.

Likewise, shaped articles are provided by the invention, whereby the polymerizable mixture of the invention may be, e.g., cast, molded, extruded or
35 injection molded, after which energy is applied to

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cause polymerization and a cured shaped article is obtained.

In yet another aspect, cured articles comprising the composition of the invention are disclosed.

5 The compositions are useful, for example, in applications requiring high performance, such as high temperature performance to 350°C or higher; in composites, particularly structural composites; structural adhesives; photodefinable adhesives; 10 vibration damping materials; electronic applications such as printed wiring boards, semiconductor encapsulants and electronic adhesives; injection molding and prepgs; and high performance binders.

By subjecting the polymerizable compositions of 15 the invention to sequential or simultaneous initiation processes via application of sufficient energy in the form of heat or light, or in any combination thereof, activated curing agents (prior exposed to energy, preferably light) can catalyze cyanate ester 20 trimerization and initiate free radical polymerization. While certain organometallic initiators are known to photoinitiate both polymerizations, the use of a separate free radical initiator for the free-radical reaction may be a more 25 efficient process.

In another aspect, the present invention provides a vibration-damping constrained-layer construction which is a laminate of one or more stiff substrates and one or more layers of a tough polymeric mixture 30 according to the present invention to damp vibrations of component parts of a device or structure. The constrained-layer construction is an integral part of, or is affixed by mechanical or adhesive means to, a solid article in need of vibration damping. These 35 constructions comprise:

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A. a stiff substrate which is any web or sheet preferably having a stiffness of at least 0.40 (relative to stainless steel) that causes it to resonate in response to an internal or external 5 applied force, and

B. a layer of viscoelastic polymer which is a polymeric network derived from polymerized ethylenically unsaturated monomers and cyanate ester monomers, so that the resulting constrained layer 10 construction has a composite loss factor, tan delta (δ) greater than or equal to 0.04 in the temperature range between -50 and 400°C and in the frequency range of 0.01 to 100,000 Hz as evaluated by a Seiko DMS 110 Rheometer using a 20 mm flexure fixture.

15 In a further aspect, the invention provides compositions which are curable pressure sensitive adhesives (PSAs). Curing of the ethylenically unsaturated component of the compositions may be accomplished by photochemical or thermal means without 20 substantially affecting the cyanate ester monomers and the cyanate ester component thus remains thermosettable. Parts may be bonded by the tacky nature of such compositions prior to cure of the cyanate ester component which may subsequently be 25 cured. The compositions provide the ease of use and green strength typical of a pressure sensitive adhesive and very high bond strengths which would be unattainable with simple PSA materials.

In another aspect, electronic adhesive materials 30 are provided which are suitable for direct chip attachment and flex circuit attachment. These are 100% solids compositions, free of any processing solvents or solvent residues. Electronic adhesives may include electrically conductive particles to 35 provide conductive adhesives. The adhesives may be tacky or tack-free depending on the application.

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In another aspect, photodefinable compositions are provided by the polymeric mixtures of the invention. Exposure of photosensitive compositions through a photographic mask allows coatings of these 5 compositions to be patterned in an image of the photomask to provide a photoresist. The photoresist may be an adhesive which may then be bonded to a variety of materials by application of heat and/or pressure. The ability to place adhesive coatings on 10 specific areas of a substrate with high image resolution may greatly simplify the manufacture of electronic devices by surface mounting techniques. The photoresist may also function as a solder mask or a patterned dielectric layer useful in defining 15 microelectronic circuits.

In yet another aspect, curable compositions comprise at least one ethylenically unsaturated monomer and as initiator certain organometallic neutral compounds. These compositions are useful in 20 the graphic arts and where improved electrical resistivity of the cured compositions is desired.

What is not taught in the prior art, but what is taught in the present invention, is the use of transition metal-containing organometallic compounds 25 and free radical generators for the simultaneous or sequential curing of cyanate monomers in the presence of ethylenically unsaturated monomers to provide polymeric mixtures possessing unique morphologies that are controllably developed thereby. There is need in 30 the art for effective high temperature vibration damping materials, as provided by the polymeric mixtures of the invention.

Problems solved by compositions of the present invention include:
35 solvents are not required;

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morphology of the cured resin can be reproducibly controlled by processing conditions as well as by choice of monomer combinations;

5 remarkable high temperature stability of acrylate containing compositions is attained by combination with cyanate ester resins;

10 excellent adhesion to polyimide film is attained; uniquely wide temperature and frequency ranges over which the cyanate ester/ethylenically unsaturated compositions are suitable for vibration damping;

15 individual cyanate ester/ethylenically unsaturated compositions can have unprecedented wide temperature and frequency ranges over which they are suitable for vibration damping;

20 excellent adhesion to metal, especially steel; the cyanate ester/ethylenically unsaturated compositions may be cured by combinations of photo and thermal processes.

In this application:

25 "catalytically-effective amount" means that amount sufficient to effect polymerization at least to a degree to cause an increase in the viscosity of the composition;

30 "cure" and "polymerize" are used interchangeably to indicate a chemical reaction in which many relatively simple molecules combine to form a macromolecule;

35 "cyanate monomer" and "cyanate ester monomer" are used interchangeably and mean a chemical substance (generally a monomer or oligomer) in which at least one -OCN group is bonded to an organic radical R through the oxygen atom, forming at least one R-OCN bond; at least two -OCN groups are preferred because of commercial availability and formation of optimized polymerized compositions;

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"energy-induced curing" means curing by means of any of electromagnetic radiation (ultraviolet and visible), electron beam, and thermal (infrared and heat) means or any combination thereof and in any sequence;

"ethylenically unsaturated" means an organic compound containing at least one carbon-to-carbon multiple bond which, on exposure to free radicals, reacts to form hydrocarbon chains;

10 "group" or "compound" or "ligand" or "monomer" or "polymer" means a chemical species that allows for substitution or which may be substituted by conventional substituents which do not interfere with the desired product; e.g., substituents can be alkyl, 15 alkoxy, aryl, halo, cyano, nitro, etc.;

"organometallic compound" means a chemical substance (ionic salt or neutral compound) in which at least one carbon atom of an organic group is bonded to a transition metal atom ("Basic Inorganic Chemistry", 20 F.A. Cotton, G. Wilkinson, Wiley, New York, 1976, p 497);

25 "IPN" refers to interpenetrating polymer networks wherein all the components are crosslinked and physically interlocked and to semi-interpenetrating polymer networks wherein only some of the components are crosslinked;

"partially polymerized syrup" and "syrup" mean a composition comprising at least one partially polymerized monomer; and

30 "radiation sensitive" means polymerizable or crosslinkable by actinic radiation (UV and visible) or electron beam.

While not wishing to be bound by theory, we postulate that compositions of the invention form 35 multiphase materials with high levels of mixing of two polymers. The mixing may create an interpenetrating

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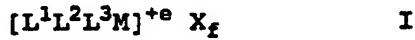
polymer network, a semi-IPN, or phase-separated morphologies of varying domain sizes. Multiphase structures are believed to provide improved toughness and increased strength. Morphologies of the inventive 5 compositions may be controlled by selection of monomers, curing agents and processing conditions.

Brief Description of the Drawing

In the accompanying Drawing, FIG. 1 is a 10 transmission electron micrograph of the invention showing a semi phase separated morphology.

Detailed Disclosure of Preferred Embodiments of the Invention

15 The present invention provides, in a preferred embodiment, a polymerizable composition comprising in the range of 70 to 30 weight percent (more preferably in the range of 60 to 40 weight percent) of at least 20 one cyanate monomer and an organometallic curing agent therefor and in the range of 30 to 70 weight percent (preferably 40 to 60 weight percent) at least one free radically polymerizable ethylenically unsaturated monomer and a curing agent therefor. The curing 25 agents for the cyanate monomers and the curing agents for the free radically polymerizable ethylenically unsaturated monomers may be independently thermally or photochemically activated. The curing agent for the cyanate monomers comprises a transition metal- 30 containing organometallic compound having the structure



35 wherein

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L^1 represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different selected from acyclic and cyclic unsaturated compounds and groups and carbocyclic aromatic and

5 heterocyclic aromatic compounds, each capable of contributing 2 to 24 pi-electrons to the valence shell of M, such as, for example, ethylene, acetylene, cyclohexadiene, eta³-propenyl, eta⁵-cyclopentadienyl, or benzene;

10 L^2 represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sigma-electrons that can be selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M, such as,

15 for example, carbon monoxide, triphenylphosphine, acetonitrile, or 2,4-pentanedione;

20 L^3 represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each M, such as alkyl, vinyl, eta¹-allyl, trimethylsilyl, acetyl, toluenesulfonyl, or triphenylstannyl;

25 M represents 1 to 6 of the same or different metal atoms selected from the elements of Periodic Groups IVB, VB, VIB, VIIIB, and VIII (commonly referred to as transition metals), such as, for example, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, and the like;

30 e is an integer having a value of 0, 1 or 2, such that the organometallic portion of the compound is neutral, cationic or dicationic;

35 each X is provided by organic sulfonates, halogenated metals or metalloids, or alkylated or arylated metal or metalloid, such as tetraalkyl borates or tetraaryl borates, or those in which X has the formula DZ_x, wherein D is a metal from Groups IB

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to VIII or a metal or metalloid from Groups IIIA to VA of the Periodic Table of Elements, Z is a halogen atom, and r is an integer having a value of 1 to 6. Preferably, the metals are copper, zinc, titanium, 5 vanadium, chromium, manganese, iron, cobalt, or nickel and the metalloids preferably are boron, aluminum, antimony, tin, arsenic, and phosphorus. Preferably, the halogen, Z, is chlorine or fluorine. Illustrative of suitable anions are BF_4^- , $\text{B}(\text{C}_6\text{H}_5)_4^-$, CF_3SO_3^- , $\text{C}_6\text{H}_5\text{SO}_3^-$, SbF_5OH^- , SbCl_6^- , PF_6^- , AsF_6^- , SbF_6^- , FeCl_4^- , SnCl_5^- , SbF_5^- , and AlF_6^- . Preferably, the anions are CF_3SO_3^- , BF_4^- , PF_6^- , SbF_6^- , SbF_5OH^- , AsF_6^- , and SbCl_6^- ; and

10 f is an integer of 0, 1 or 2, the number of anions required to balance the charge e on the 15 organometallic portion of the structure of Formula I; with the proviso that the organometallic compound contains at least one transition metal-carbon bond; and with the proviso that L^1 , L^2 , L^3 , M, e, X, and f 20 are chosen so as to achieve a stable configuration.

Preferred organometallic compounds according to formula I are:

25 $[\text{CpFe}(\text{CO})_2]_2$, $\text{Mn}_2(\text{CO})_{10}$, $[\text{CpMo}(\text{CO})_3]_2$, $[\text{CpW}(\text{CO})_3]_2$, $\text{Re}_2(\text{CO})_{10}$, $[\text{CpMo}(\text{CO})_2\text{PPh}_3]_2$, $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$, $\text{Fe}_3(\text{CO})_{12}$, $\text{CpFe}(\text{CO})_2\text{SnPh}_3$, $(\text{CO})_5\text{MnSnPh}_3$, $\text{Cp}(\text{CO})_3\text{Fe}(1+)\text{PF}_6(1-)$, $(\eta^6\text{-benzene})\text{CpFe}(1+)\text{PF}_6(1-)$, $(\eta^6\text{-mesitylene})\text{CpFe}(1+)$, $\text{BF}_4(1-)$, bis($\eta^6\text{-mesitylene}$) $\text{Fe}(2+)\text{SbF}_6(1-)$, $(\text{MeCp})\text{Mn}(\text{CO})_3$, $\text{CpMn}(\text{CO})_3$, $\text{CpFe}(\text{CO})_2\text{Cl}$, $[(\text{p-cymene})\text{RuCl}_2]_2$, $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$, wherein

30 Me is methyl,
Ph is phenyl,
Cp is η^5 -cyclopentadienyl,
Cp* is η^5 -pentamethylcyclopentadienyl, and
MeCp is η^5 -methylcyclopentadienyl.

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Cyanate monomers that can be polymerized using the curing agent of the present invention contain at least two -OCN groups, and are of the general formula



II

wherein p can be an integer from 2 to 7, and wherein Q comprises at least one of 1) a di-, tri-, or tetravalent aromatic hydrocarbon group containing 5 to 10 carbon atoms, wherein 1) optionally comprises at least one of 1 to 5 aliphatic or polycyclic aliphatic divalent hydrocarbon groups containing 7 to 20 carbon atoms and 1 to 10 heteroatoms selected from the group consisting of non-peroxidic oxygen, sulfur, non-phosphino phosphorus, non-amino nitrogen, halogen, silicon, and 2) a divalent fluorocarbon group having 3 to 12,500 carbon atoms and 5 to 25,000 fluorine atoms corresponding to formula III:



III

where B is 1) a carbon-to-carbon bond, in which case a is an integer of 1 to 30 and b is zero, or 2) B is $[(CFY)_dO(CFY)_e]_w$, in which case a and b are zero, d and e are integers of 1 to 30, and w is an integer of 1 to 20, or 3) B is $(OCF_2-CFY)_gO(CFY)_hO(CFY-CF_2O)_i$, in which case a and b are 1, h is an integer of 1 to 10, and g and i are integers of 1 to 100, or 4) B is $[(CF_2CH_2)_j(CF_2-CFY)_k]_m$, in which case a and b are integers of 1 to 10, j and k are integers whose ratio j/k is 1/1 to 1/10, m is an integer of 1 to 100, and (CF_2CH_2) and (CF_2-CFY) are randomly distributed units; and where Y is fluorine or perfluoroalkyl of 1 to 10 carbon atoms.

35 In the practice of this invention, preferably a combination of cyanate monomers is used whereby such

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combination is comprised of one or more cyanates of Formula II where p is an integer 2 to 7, and optionally one or more monofunctional cyanates (e.g. Formula II where p is one). Examples of cyanates are 5 as follows: cyanatobenzene, 4-cyanatobiphenyl, 1,3- and 1,4-dicyanatobenzene, 2,4-dimethyl-1,3-dicyanatobenzene, 4-chloro-1,3-dicyanatobenzene, 1,3,5-tricyanatobenzene, 2,2'- or 4,4'-dicyanatobiphenyl, 3,3',5,5'-tetramethyl-4,4'- 10 dicyanatodiphenyl, 1,3-, 1,4-, 1,5-, 1,6-, 1,8-, 2,6-, or 2,7-dicyanatonaphthalene, bis(4-cyanatophenyl)methane, bis(3-chloro-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)propane, 1,1,1-tris(4- 15 cyanatophenyl)ethane, 1,1-bis(4-cyanatophenyl)ethane, 2,2-bis(3,5-dibromo-4-cyanatophenyl)propane, bis(4-cyanatophenyl)ether, bis(4-cyanatophenyl)thioether, bis(4-cyanatophenyl)sulfone, tris(4-cyanatophenyl)phosphite, and 20 tris(4-cyanatophenyl)phosphate.

Essentially, any phenol derivative reactive towards cyanogen halide in the presence of base is within the scope of the invention. Monomeric phenol derivatives include, for example, resins designated as 25 B-10, L-10, M-10 and RTX-366 (also available from Ciba-Geigy). It is also well known in the art that cyanate monomers can be partially prepolymerized to yield soluble oligomers. These oligomers may also be used as the cyanate monomers in this invention. Such 30 oligomers are commercially available as B-30TM, B-50TM, M-20TM, M-30TM, and T-30TM cyanate ester resins (Ciba-Geigy).

Ethylenically unsaturated monomers useful in the present invention preferably can be selected from 35 acrylate, methacrylate, and vinyl ester functionalized materials that are capable of undergoing free radical

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polymerization. Of particular use are acrylate and methacrylate materials. They can be monomers and/or oligomers such as (meth)acrylates, (meth)acrylamides, N-vinylpyrrolidone and vinylazlactones. Such monomers 5 include mono-, di-, or polyacrylates and methacrylates such as methyl methacrylate, n-butyl acrylate, isooctyl acrylate, isobornyl acrylate, isobornyl methacrylate, acrylic acid, tetrahydrofurfuryl acrylate, N-vinylcaprolactam, N-vinylpyrrolidone, 10 acrylonitrile, glycerol diacrylate, and triacrylate, ethylene glycol diacrylate, 1,6-hexanediol diacrylate, 1,3-propanediol diacrylate and dimethacrylate, trimethylolpropane triacrylate, 2-phenoxyethyl acrylate, pentaerythritol triacrylate, 15 2,2-bis[1-(3-acryloxy-2-hydroxy)]propoxyphenylpropane, tris(hydroxyethyl)isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight average 200-500, copolymerizable mixtures of mono-, di-, and tri- 20 (meth)acrylated isocyanurates and poly(meth)acrylated aliphatic alkyl (poly)isocyanates, and acrylated oligomers such as polyester polyols of average molecular weight between 900 and 6000 having terminal (meth)acrylate groups.

25 It may be desirable to crosslink the ethylenically unsaturated components of the polymerizable compositions of the invention. Particularly useful as crosslinker compounds are acrylates such as glycerol diacrylate and triacrylate, 30 ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,3-propanediol diacrylate and dimethacrylate, trimethylolpropane triacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol 35 triacrylate, tetraacrylate, and tetramethacrylate, and the bis-acrylates and bis-methacrylates of

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polyethylene glycols of average molecular weight 200-500.

Organometallic compounds of formula I having one L¹ ligand, 1 to 6 L² ligands, no L³ ligands and one metal M as defined previously (i.e., the organometallic compounds have the formula [L¹L²M]) and wherein e and f of formula I are zero, surprisingly are photocatalysts for the cure of the ethylenically unsaturated monomers of the invention. Illustrative examples include MeCpMn(CO)₃, (C₆H₆)Cr(CO)₃, (MeC₆H₅)Cr(CO)₃, (MeOC₆H₅)Cr(CO)₃, (C₆H₆)W(CO)₃, CpMn(CO)₃, and Cp*Mn(CO)₃, wherein Me, Cp, MeCp, and Cp* are as previously defined. As is known in the art, this class of organometallic compounds can also act as catalysts for cyanate ester polymerization. Compositions comprising an ethylenically unsaturated monomer and a cyanate ester monomer using this unique class of organometallic compounds as initiator can be useful as noted herein for mixed polymer networks.

Other free radical curatives useful for the polymerization of the ethylenically unsaturated monomers include organic peroxides such as benzoyl peroxide and di-*t*-butylperoxide, azo compounds such as azobisisobutylnitrile (AIBN), benzoin ethers such as benzoin-iso-propyl ether and benzoin-*n*-butyl ether, acetophenones such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone, onium salts such as diphenyliodonium and triphenyl sulfonium salts, ketals such as benzildimethyl ketal, benzophenone, isopropylthioxanthone, ethyl-4-(dimethylamino)benzoate, and other free radical curatives known to those skilled in the art. The free radical curatives may be photochemically or thermally activated. Preferred thermally activated free radical curatives include azo-*t*-butane, 2,2'-azobis(2,4,4-trimethyl-pentane), di-*t*-butyl peroxide, and 1,1-di-

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(*t*-butylperoxy)-3,3,5-trimethylcyclohexane.

Photochemically activated free radical curatives are preferred and of these benzildimethyl ketal (EsacureTM KB1 from Sartomer Company) is most preferred.

5 It may be desirable, and in some embodiments it is preferred, to partially prepolymerize at least one of the free-radically polymerizable monomers or to prepolymerize at least one of the cyanate ester monomers to aid in processing and to effect changes in
10 the physical properties of the cured compositions.

There are two methods for preparing partially prepolymerized syrups of the ethylenically unsaturated monomers described below as Methods A and B. The methods may be used individually or in combination.

15

Method A

The syrup is prepared by

20 1) mixing the polymerizable cyanate ester and ethylenically unsaturated monomers with an effective amount of a free radical initiator (usually 0.01 to 5.0% by weight of total monomers, preferably 0.02 to 1.0% by weight of total monomers);

25 2) applying energy to the mixture to effect partial polymerization such that the Brookfield viscosity is increased to within a range of 300 to 20,000 centipoise at ambient temperature, preferably 500 to 4000 centipoise. Preferably, the applied energy is UV light and the free radical initiator is a photoinitiator;

30 3) admixing at least one organometallic compound, along with optional crosslinkers, adjuvants, bireactive monomers, or stabilizers; and

35 4) degassing the curable compositions under vacuum to remove dissolved air and oxygen.

35 Preferably, degassing is carried out just prior to

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coating. If stored, the degassed compositions should be kept from exposure to light.

Method B

- 5 When a mixture of more than one alkyl (meth)acrylates is used as the ethylenically unsaturated component, the syrup is made as follows:
 - 1) mixing the ethylenically unsaturated monomers with an effective amount of a free radical
 - 10 initiator (usually 0.01 to 5.0% by weight of total monomers, preferably 0.02 to 1.0% by weight of total monomers);
 - 15 2) applying energy to the mixture to effect partial polymerization such that the Brookfield viscosity is increased to within a range of 300 to 20,000 centipoise at ambient temperature, preferably 500 to 4000 centipoise. Preferably, the applied energy is UV light and the free radical initiator is a photoinitiator. Low intensity irradiation and cooling
 - 20 25 minimize gel formation during the syrup making process;
 - 3) in a separate container, mixing the cyanate ester monomer and the organometallic catalyst, optionally with the use of an appropriate solvent and/or heat;
 - 4) mixing the alkyl (meth)acrylate syrup and the cyanate ester mixture, along with any optional additives, adjuvants, bireactive monomers, or crosslinkers;
 - 30 5) degassing the curable compositions under vacuum to remove dissolved air or oxygen. Preferably, degassing is carried out just prior to coating. If stored, the degassed compositions should be kept from exposure to light.

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The preferred method is to combine two or more ethylenically unsaturated syrups, wherein each syrup is prepared either using Method A or Method B.

Photoinitiators which are useful for preparing a 5 partially polymerized syrup include compounds such as the benzoin ethers (such as benzoin methyl ether), substituted benzoin ethers (such as anisoin methyl ether), substituted acetophenones (such as 2,2-dimethoxy-2-phenylacetophenone), and substituted 10 alpha-ketols (such as 2-methyl-2-hydroxypropiophenone).

Another group of monomers which are useful in compositions of the invention are bireactive monomers which serve as co-crosslinkers, i.e., those that 15 possess at least one free-radically polymerizable group and one cyanate ester or cyanate ester-reactive functionality. A cyanate ester-reactive functionality is a group capable of entering into a chemical reaction with a cyanate ester group. Examples of 20 cyanate ester-reactive functionalities include cyanate ester, alcohol, primary amine, secondary amine, and thiol groups. Bireactive monomers include, for example, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl 25 acrylate, 4-cyanatophenyl styrene, and 4-cyanato(allyl)benzene. Bireactive monomers can comprise up to 50 weight percent, preferably less than 25 weight percent, of the curable composition. Most preferably, the compositions are free of bireactive 30 monomers.

Organic solvents can be used to assist in dissolving the photoinitiator system in the ethylenically unsaturated monomers and cyanate ester monomers and as a processing aid. Representative 35 solvents include polar or nonpolar organic solvents such as propylene carbonate, sulfolane, methyl ethyl

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ketone, methylene chloride, nitromethane,
acetonitrile, gamma-butyrolactone, and
1,2-dimethoxyethane (glyme). The photoinitiator may
also be sorbed onto an inert support such as silica,
5 alumina, and clays.

Free radical polymerization preferably is carried
out in an inert atmosphere such as nitrogen, carbon
dioxide, helium or argon. A sufficiently inert
atmosphere can be achieved by covering a layer of the
10 polymerizable mixture with a plastic film; for
photoactive compositions this film should be
transparent to ultraviolet radiation. The composition
should be kept in low light, or preferably total
darkness, in air, vacuum, or inert gaseous atmosphere
15 until ready for polymerization.

Curing agents can be present in the range of 0.01
to 20, preferably 0.1 to 10 weight percent of the
total composition.

The present invention also provides a process for
20 the polymerization of a combination of cyanate ester
monomers and ethylenically unsaturated monomers,
comprising the steps of:

(a) providing at least one cyanate ester monomer
and at least one ethylenically unsaturated monomer;
25 (b) adding to said mixture a catalytically
effective amount of a cyanate ester curing agent
comprising an organometallic compound and a
catalytically effective amount of a free radical
curing agent comprising an organic compound capable of
30 generating free radicals (and all permutations of the
order of mixing the aforementioned components),
thereby forming a polymerizable mixture, and
(c) allowing the mixture to polymerize or adding
energy to the mixture to effect polymerization.

35 Where divided, the steps are preferably arranged
as follows:

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- 1) mixing ethylenically unsaturated monomer(s) with an effective amount of a free radical generating curing agent and any optional bireactive monomers except as noted in step 3 (below);
 - 5 2) applying energy to effect polymerization such that Brookfield viscosity is increased to within a range of 300 to 20,000 centipoise at ambient temperature, preferably 500 to 4000 centipoise. Alternatively, viscosity can be increased by partial
 - 10 10 polymerization in the presence of thermal initiator(s) or organometallic initiator(s), or by mixing with a viscosity-adjusting agent such as hydrophilic silica;
 - 15 3) admixing bireactive cyanate ester monomers; and
 - 15 4) admixing cyanate ester monomers.
- 20 The organometallic initiator, crosslinking agent, and an additional amount of free radical initiator may preferably be added at any time after the second step polymerization. The initiators may be mixed with any component. The finished modified syrup may be coated onto a backing and exposed to energy to complete the polymerization.
- 25 Alternatively, the composition may be made by mixing all monomers except the cyanate ester with an effective amount of a free radical initiator, partially polymerizing to increase viscosity, then adding the organometallic curing agent, crosslinking agent, additional free radical initiator, and the cyanate ester, and following up by a sequential or
- 30 30 simultaneous initiation process.
- 35 In still an additional method, step one can be omitted, and all monomers and crosslinking agent can be mixed with a free radical initiator and an organometallic initiator, followed by a sequential or simultaneous initiation process.

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In one embodiment, it is preferred to combine two or more ethylenically unsaturated polymerizable syrups, wherein each syrup is separately prepared using any of the methods disclosed herein. Processing 5 to provide high performance compositions is assisted when in the range of 1 to 50 weight percent (or that weight percent present up to the gel point of the composition) of monomers are prepolymerized into a syrup. Preferably, 1 to 30 weight percent, and most 10 preferably 1 to 15 weight percent of monomers are prepolymerized.

It may be desirable to add solvent to solubilize components and aid in processing. Solvent, preferably organic solvent, in an amount up to 99 weight percent, 15 but preferably in the range of 0 to 90 weight percent, most preferably in the range of 0 to 75 weight percent, of the polymerizable composition can be used. Most preferably, the polymerizable composition is solvent-free.

20 In general, thermally induced polymerization of cyanate monomers with organometallic catalysts may be carried out at 80 to 250°C (preferably 80 to 150°C). In general, radiation-induced polymerization of cyanate monomers with latent curing agents comprising 25 an organometallic compound can be carried out at 80 to 125°C for the majority of energy curable compositions, although low temperature (e.g., 25 to 80°C) or elevated temperature (e.g., 125 to 300°C, preferably 125 to 200°C) can be used to subdue the exotherm of 30 polymerization or to accelerate the polymerization, respectively. In some instances it is desirable to use a two-stage cure: curing at a low temperature (e.g., 25 to 80°C) to gel the composition followed by a high temperature post cure (e.g., above 80 to 300°C) 35 to develop the final properties of the composition. Temperature of polymerization and amount of catalyst

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will vary and be dependent on the particular curable composition used and the desired application of the polymerized or cured product. The amount of curing agent to be used in this invention should be

5 sufficient to effect polymerization of the monomers or precursors (i.e., a catalytically-effective amount) under the desired use conditions. Such amount generally will be in the range of about 0.01 to 20 weight percent, and preferably 0.1 to 10.0 weight

10 percent, based on the weight of curable composition.

For those compositions of the invention which are radiation-sensitive, any source of radiation including electron beam radiation and radiation sources emitting active radiation in the ultraviolet and visible region

15 of the spectrum (e.g., about 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, xenon lamps, lasers, sunlight, etc. The required amount of exposure to effect polymerization is

20 dependent upon such factors as the identity and concentration of catalysts, the particular cyanate ester and ethylenically unsaturated monomers, the thickness of the exposed material, type of substrate, intensity of the radiation source and amount of heat

25 associated with the radiation.

Thermal polymerization using direct heating or infrared electromagnetic radiation, as is known in the art, can be used to cure polymerizable compositions according to the teachings of this invention.

30 It is within the scope of this invention to use multiple wavelengths of actinic radiation by irradiating the photopolymerizable compositions sequentially. In the preferred method, photopolymerization is effected by sequential exposure

35 to a radiation source emitting active radiation in the visible region of the spectrum, followed by exposure

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to a radiation source in the ultraviolet region of the spectrum. It is also preferred to heat either during or after irradiation in the visible region. In addition, it may be desirable to subsequently

5 thermally polymerize the activated precursor so obtained, the irradiation temperatures being below the temperature employed for subsequent heat postcuring. These activated precursors may normally be polymerized at temperatures which are substantially lower than
10 those required for direct thermal polymerization, with an advantage in the range from 50 to 110°C. This process also makes it possible to control polymerization in a particularly simple and advantageous manner.

15 It is within the scope of this invention to include two-stage polymerization (curing), by first activating curing agent by irradiating the curable compositions and subsequently thermally curing the activated precursors so obtained. Activated
20 compositions may normally be cured at temperatures in the range of 50 - 150°C lower than those for direct thermal curing.

Adjuvants such as solvents, pigments, abrasive granules, stabilizers, light stabilizers,
25 thermoplastics, antioxidants, flow agents, bodying agents, flattening agents, colorants, inert fillers, binders, blowing agents, fungicides, bactericides, surfactants, plasticizers, conductive particles, and other additives as known to those skilled in the art
30 can be added to the compositions of this invention. These can be added in an amount effective for their intended purpose.

Compositions of this invention may be applied, preferably as a liquid, to coat a variety of
35 substrates including metal such as steel, aluminum, copper, cadmium, and zinc; glass, paper, wood, or

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various plastic films such as polyimide, poly(ethylene terephthalate), plasticized poly(vinylchloride), poly(propylene), or poly(ethylene), followed by irradiation. Irradiation through, e.g., a photomask, 5 selectively polymerizes portions of the coating, and the unexposed portions can be removed by, e.g., a solvent wash. Thus, articles useful in the graphic arts such as printing plates and printed circuits may be produced. Such methods are well known in the art 10 (see for example British Patent Specification No. 1,495,746).

The present invention composition can have utility as a vibration damping material. Properties of vibration-damping materials are described in the 15 literature. Nielsen, L.E., Mechanical Properties of Polymers, Van Nostrand Reinhold: New York, 1965; pp 162-165, discloses that materials possessing the maximum vibration-damping capability have shear storage moduli, G' , greater than 10^7 dynes/cm² but less 20 than 10^{10} dynes/cm² at the use temperature. Furthermore, Rosen, S.L., Functional Principles of Polymeric Materials for Practicing Engineers; Barnes and Noble: New York, 1971; pp 222-227, shows that it 25 is desirable for a vibration-damping material to have both a storage modulus and a loss tangent with values as high as possible.

Yerges, L.F., Sound, Noise, and Vibration Control; Van Nostrand Reinhold: New York, 1965; pp 68-69, notes that useful damping materials exhibit 30 decay rates from as low as 5 to 80 dB/sec (decibels/second), and from 1/2 to 20 percent of critical damping. ("Critical" damping is the damping necessary to just prevent oscillation).

Damping materials are applied to structures and 35 component parts in devices to attenuate resonant vibrations and thereby reduce noise and vibrational

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fatigue. The ability of a material to damp is measured by its ability to convert vibrational energy to heat energy. In viscoelastic materials, this occurs most effectively at the glass-rubber transition 5 temperature. The effectiveness of a viscoelastic material in energy dissipation can be evaluated by measuring its viscoelastic response to a periodic stress or strain, specifically the amount of the viscous lag between the imposed stress wave and the 10 induced strain wave. The Youngs Modulus, E^* , of a material is a complex number, given by the sum of the storage and dissipation (or loss) terms: $E^* = E' + iE''$. The dissipation term, E'' , is a measure of how much energy a material can damp or dissipate. The 15 shear modulus, G^* , is similarly defined as $G^* = G' + iG''$. The lag, known as δ , is the measure in degrees of how much out of phase the stress and strain are. The tangent of δ , frequently referred to as the dissipation (or loss) factor, is defined by the ratio 20 of the loss modulus to the storage modulus: $\tan \delta = E''/E'$ or $\tan \delta = G''/G'$. Viscoelastic materials in the glass transition regime could have a large energy dissipation contribution to the modulus, and thus have a large $\tan \delta$. Results of dynamic mechanical analysis 25 (DMA) tests are generally given in terms of the storage modulus, E' or G' , the loss modulus, E'' or G'' , and $\tan \delta$. $\tan \delta$ is a damping term and is a measure of the ratio of energy dissipated as heat to the maximum energy stored in the material during one cycle 30 of oscillation. The morphologies of cured resin compositions of the invention are reflected by the shape of the $\tan \delta$, E' , E'' , G' , or G'' curves obtained by DMA; a single phase system gives a single $\tan \delta$ peak while a multiphase system will give multiple or 35 broadened $\tan \delta$ peaks.

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IPNs and semi-IPNs are attractive classes of materials because they have a potential of offering toughened high performance materials with superior adhesive properties (up to at least 800 g/mm² shear value) from common and inexpensive polymers and monomers. IPNs have the ability to provide materials with vastly differing properties and performance using the same starting components via the variation of the ultimate IPN morphology. Morphology describes the 10 micro- and macro-molecular architecture, i.e., how intimately the components are mixed on a continuum of size scales. The ability to control this IPN morphology provides for high performance polymers at low cost.

15 While not wishing to be bound by theory, it is believed that, for ideal vibration damping constructions, the elastomeric polymeric IPN should exhibit the morphology of a semi-phase separated or microheterogeneously phase separated IPN. Such 20 materials exhibit an aggregate molecular architecture consisting of a continual spectrum of compositions, ranging from pure low-Tg homopolymer to pure high-Tg homopolymer. The tan δ curve from DMA of such a material will tend to show one very broad peak roughly 25 spanning the temperature range between the glass transition temperatures of the two component homopolymers. Ideally, the tan δ of such an IPN, as measured by DMA in the constrained layer mode, will be at least 0.03 as measured across at least 20% of the 30 temperature range between the Tg of the pure high-Tg component and that of the pure low-Tg component.

Control over the morphology of an IPN arises from the ability to control the rates of diffusion and polymerization of the respective monomers, the 35 polymerization process itself (order of mixing, order of polymerization, curing energy, rate of

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polymerization, time interval between polymerization of each monomer, etc.), choice of initiator(s), and the use of additives. The organometallic catalysts used for cure of the cyanate component of the present 5 invention also initiate some degree of cure of the ethylenically-unsaturated monomers, thus greatly affecting the development of microheterogeneously phase-separated IPNs of this invention.

FIG. 1 is a transmission electron micrograph of a 10 polymerized mixture comprising a combination of isooctyl acrylate, isobornyl acrylate, cyanate ester Quatrex-7187, and as curative $[\text{CpFe}(\text{CO})_2]_2$ and benzoin dimethylketal which shows a semi phase separated IPN structure 10. Microheterogeneous phases of 15 polymerized cyanate ester-acrylate regions 2, which are cyanate ester rich, are incorporated in polymerized acrylate-cyanate ester region 4, which is acrylate rich, and provides high performance properties to the IPN. The cyanate rich regions have 20 been stained with ruthenium tetroxide to enhance their visibility.

The desired semi-phase separated morphology may also be defined as a cured or partially cured composition in which $\tan \delta$, as measured by DMA in the 25 constrained layer mode, is at least 0.03 over 20% or more of the temperature range between the T_g of the pure high T_g component and the T_g of the pure low T_g component.

Control over the morphology of an IPN is a result 30 of the ability to control the rates of diffusion and polymerization. Partial prepolymerization of components, individually or together, provides additional control of these rates. The control is multi-fold: the rates can be varied by the choice of 35 materials, processing and catalytic systems. The materials ch ice can affect the vis osity or th

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rigidity of the polymerizing composition via the degree of cross-linking and the Tgs of the selected individual components. Compositions of different viscosities provide differing barriers to both 5 diffusion and propagation. Also, by varying the relative amounts of the low Tg acrylate in the composition, the Tg range of the ultimate IPN can be shifted.

Processing can greatly affect the rates by simply 10 changing the order in which the IPN components are polymerized. The energy used to cure the components can be adjusted to affect the rates. Thermal cure can be substituted for the photoactivated polymerization to change the pace of the polymerization. Processing 15 can be used to adjust the amount of time which passes between the initiation of each cure, thus allowing greater degree of diffusion and therefore, phase separation.

Choice of catalysts or initiators and amount used 20 can have a profound effect on the polymerization and its speed. The organometallic catalysts used for cure of the cyanate component of compositions of this invention also initiate some degree of cure of the ethylenically unsaturated monomers. This ability to 25 cause some simultaneous cure of both components with one catalyst can be a key feature in the development of the microheterogeneously phase separated IPNs of this invention. Additives can be used to delay or speed up cure of the polymer.

30 As is known in the art, the most efficient use of a damping material occurs if the material is sandwiched between the article to be damped and a relatively stiff layer, such as a thin metal sheet. This forces the damping material into shear as the 35 article vibrates, dissipating substantially more energy than when the material acts simply in extension

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and compression. This is commonly known as a constrained layer construction.

A suitable material for a stiff substrate has a stiffness of at least 0.40 (relative to stainless 5 steel) as defined in Handbook of Tables for Applied Engineering Science, Bolz, R.E. et al., eds., CRC Press: Cleveland, Ohio, 1974, p 130. The desired stiffness of the substrate is varied by adjusting its thickness, for example from about 25 micrometers to 5 10 centimeters, depending on the modulus of the substrate. Examples of suitable materials include metals such as iron, steel, aluminum, copper and alloys thereof; stiff polymeric materials such as polystyrene, polyvinylchloride, and polycarbonate; 15 fiber-reinforced plastics such as glass fiber, ceramic fiber, and metal fiber-reinforced polyester; and ceramics.

Solid articles comprising viscoelastic polymeric mixtures of the invention are prepared by either of 20 two processes. In a first process, a layer of the polymerizable mixture is coated onto a release liner, the mixture is polymerized, and the layer of resulting polymeric mixtures transferred to a stiff substrate and adhered thereto, thereby providing a 25 constrained-layer construction. In the second process, a layer of the polymerizable mixture is coated directly onto a stiff substrate and the mixture polymerized *in situ* thereby also providing a constrained-layer construction. The constrained-layer 30 construction is then mechanically (e.g., as by bolting) or adhesively affixed to a solid article that requires vibration damping. Alternatively, the vibration damping layer may be an integral part of the article requiring damping, such as an automotive body 35 panel or a disc brake pad assembly. When the solid article subsequently vibrates under the influence of

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an internal or external applied force, vibration in the solid article is damped. The process for polymerization of the composition may be completed in one step, or may be divided into several steps
5 separated by an interval of time, where such is preferable.

Since the viscoelastic polymer often has adhesive properties, the polymer can usually be adhered to a substrate without the use of an adhesive. It is
10 sometimes desirable, however, to use a thin layer (e.g., 20-50 μm) of high-modulus adhesive, such as an acrylic adhesive or an epoxy adhesive, to bond the polymer to a solid article which can be, for example, an oil pan, a valve cover, or a transmission housing.
15 Vibration damping materials of this invention are particularly useful in high temperature applications and in applications requiring damping over very broad temperature ranges. Damping from less than 0°C to over 300°C are possible with single compositions of
20 this invention.

The cyanate ester/ethylenically unsaturated compositions of this invention exhibit improved thermal stability, surviving multi-hour exposures to 260°C. The damping ability of some compositions
25 improved upon repeated thermal cycling to 300°C.

The wide temperature damping range and excellent thermal stability of the compositions of this invention make these materials useful as sound dampers for automotive brake shoes. Such applications
30 typically require damping from ambient temperatures to about 150°C combined with the ability to withstand 260°C for two hours. The action of the brake piston during the braking requires the polymeric damper constrained between metal plates to withstand over
35 350 g/mm² (500 lb/in²) in shear. Mass production of such constrained layer geometries further requires

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solution coating or tape laminating of the damping materials onto a metallic sheet that is wound into a coil. The constrained layer damping construction desirably has a T-peel adhesion exceeding 90 g/mm

- 5 (5 lb/in) in order to resist degradation during these winding processes. Cyanate ester/acrylate compositions are preferred for these types of rigorous applications. The fine degree of control over intermediate and final morphologies allows a room
- 10 temperature viscoelastic material to have semi-structural overlap shear, excellent thermal stability, and good T-peel adhesion. For a brake shoe damper, the best morphology is obtained by a three step process; a short thermal cure, followed by a
- 15 photocure, with a final thermal cure at a temperature higher than the initial thermal cure. The preferred cyanate resin is Quatrex-7187™ (Dow Chemical Co.), the preferred acrylate is a mixture of isobornyl acrylate syrup and isoctyl acrylate syrup, and the preferred
- 20 curatives are benzildimethyl ketal and $[\text{CpFe}(\text{CO})_2]_2$.

For most applications, the layer of viscoelastic polymer is a coating having a thickness of at least 0.01 mm up to about 100 mm, preferably 0.025 to 100 mm, and most preferably 0.05 to 100 mm. The coating

- 25 can be applied by any of the techniques known in the art such as by spray, dip, knife, or curtain coating.

The polymerizable (curable) mixtures of the invention can be used to provide a pressure sensitive adhesive, which when coated onto a flexible backing

- 30 provides a tape, or when the flexible backing has release properties there is provided a transfer tape.

The adhesives of the invention useful in electronic applications (referred to as electronic adhesives) may be produced by combining an effective

- 35 amount (preferably 20 to 80 weight percent, more preferably 30 to 70 weight percent, and m st

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preferably 40 to 60 weight percent of the total composition) of a cyanate ester monomer or oligomer, a curing catalyst for the cyanate ester, an effective amount (preferably 80 to 20 weight percent, more 5 preferably 70 to 30 weight percent, and most preferably 60 to 40 weight percent of the total composition) of an ethylenically unsaturated monomer or prepolymer, a free radical generating curative, and various desirable additives such as electrically 10 conductive particles, thermoplastics, and coupling agents. Combinations of cyanate ester resins and ethylenically unsaturated resins (monomers or partially polymerized resins) are chosen such that a homogeneous solution is obtained which has a viscosity 15 suitable (preferably 300 to 20,000 cps, most preferably 500 to 4000 cps) for coating operations.

The catalyst system of organometallic curative and free radical generators may be activated thermally or photochemically or in any combination. It is 20 preferred that one of the catalysts be photochemically activated and the other be thermally activated. Most preferably, the cyanate ester curative is a thermally activated catalyst such as $[\text{CpFe}(\text{CO})_2]_2$, wherein Cp is cyclopentadienyl, and the free radical generator is a 25 photoactive material such as benzildimethyl ketal. The adhesive can be coated by standard techniques between two release liners, such as polypropylene or silicone treated polyester, and the ethylenically unsaturated resin is cured by the application of heat. 30 or, preferably, light to give an adhesive film wherein the cyanate portion remains as a thermosettable resin. When the ethylenically unsaturated resin component of the film is photochemically cured, at least one of the release liners must be transparent to the wavelength 35 of light used to effect the cure. Alternatively, the compositions may be coated onto a single release liner

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and thermally or photochemically cured under an inert, oxygen free atmosphere such as nitrogen.

It is preferred that no solvents are used in the coating and processing of the electronic adhesive of 5 the invention. In use, the adhesive film, which may be tacky or non tacky depending upon the resins chosen, is placed between the surfaces to be bonded, such as flex circuitry and printed circuit boards, and laminated by the application of heat and pressure. 10 Electrical contact may be made by metallic features on the substrates to be bonded which protrude through the adhesive film during the bonding step (as with a "bumped" chip). Alternatively, the adhesive can be loaded with electrically conductive particles as 15 described in U.S. Patent No. 5,143,785, col. 7, line 58 to col. 8, line 15, such that no electrical conductivity is possible in the plane of the film but electrical conductivity is provided through the thickness of the film; such materials are referred to 20 as Z-axis Films (ZAF).

Any of several electrically conductive particle types may be used in the invention and are selected based on the intended application. Examples of useful particle types include metalized plastic spheres, 25 solid metal particles, precious metal coated metal particles, solder particles and graphite powders. Particles having diameters in the range of 2-30 micrometers are preferred with 10-20 micrometer diameters being most preferred. Particle loadings in 30 the range of 1-25% by volume of the adhesive are preferred with 2-10% as the most preferred range.

Acrylates are the preferred ethylenically unsaturated monomers and isooctyl acrylate, isobornyl acrylate, phenoxyethyl acrylate, butyl acrylate, and 35 tetrahydrofurfuryl acrylate are particularly useful. Because polyimide flex circuitry is of great

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importance in the electronics industry, adhesion to polyimide is critical. It is thus desirable additionally to incorporate acrylates containing basic or nitrogenous functionality such as dimethyl 5 acrylamide, *N*-vinyl caprolactam, *N*-iso-butoxymethyl acrylamide, cyclohexylmaleimide, and *N*-*t*-butylacrylamide into the electronic adhesive compositions to promote adhesion to polyimide substrates. It may also be desirable to incorporate 10 di- or polyfunctional acrylates such as 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, pentaerythritol triacrylate, urethane acrylate CN 962™ from Sartomer Co., urethane methacrylate CN 974™ from Sartomer Co., and epoxy acrylate CN 104™ from Sartomer 15 Co., to partially crosslink the acrylate portion of the composition. Useful cyanate esters resins have been noted above. Preferred cyanate ester resins include B-30™, M-20™, RTX-366™, PT-30 and Quatrex-7187™. Adhesive formulations will determine the 20 properties thereof. For example, when the combined amount of cyanate ester monomer and polyfunctional ethylenically unsaturated monomer is in the range of 20 to 70 weight percent of total monomer content, bonds that are formed may be debonded by heat and 25 solvent treatment without damage to the electronic components. The parts may then be rebonded and electrical connections restored. Higher levels of cyanate ester monomers provide permanent (i.e., not reworkable) bonds. Preferably, the bonds will be 30 reworkable, such that the combined amount of cyanate ester monomer and polyfunctional ethylenically unsaturated monomer is in the range of 30 to 60 weight percent.

Other additives such as coupling agents, inert 35 fillers, and thermoplastic resins may be included for

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their intended purposes, generally in amounts up to 50 weight percent.

Since the ethylenically unsaturated portion of the compositions of the present invention can be cured substantially independent of the cyanate ester portion, it is possible to prepare curable pressure sensitive adhesives with these compositions. Acrylates are particularly useful as the ethylenically unsaturated monomer when preparing curable pressure sensitive adhesives. The ethylenically unsaturated monomer(s) and cyanate ester monomer(s) are chosen such that upon cure of the ethylenically unsaturated monomer, a tacky film is obtained. A non-tacky film could also be used provided it becomes tacky at elevated temperatures where it can then be applied to the surfaces to be bonded. The films may be free standing, coated on a release liner, or coated on a backing such as paper, cloth, polymer, or metal. This may then be used to bond two substrates together by the PSA nature of the composition, subsequent application of energy, preferably heat, cures the cyanate ester portion to provide a bond of higher strength than the bond containing uncured cyanate ester resin. The compositions offer the convenience of a PSA while ultimately providing very high bond strengths not typically available from a standard PSA. Acrylates and cyanates which are particularly useful in curable PSA compositions of this invention have been noted above. The curable PSA compositions may contain 5-95% cyanate ester monomer and 95-5% acrylate monomer. Preferred compositions contain 20-80% cyanate and 80-20% acrylate by weight, and the most preferred compositions contain 35-65% cyanate and 65-35% acrylate by weight.

In an alternative method, the cyanate ester/ethylenically unsaturated composition may be

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applied as a coating, via various standard coating techniques, to a first substrate prior to curing. The ethylenically unsaturated component may then be cured by exposure to energy in the form of heat or light,
5 preferably light, to provide a curable PSA coating. The first substrate is then bonded to a second substrate via the curable PSA after which the application of heat and pressure provides the bonded article. It is preferred that the curable PSA be
10 applied to the first substrate at ambient temperature (15-35°C) but lower and higher temperatures may be used. The preferred curing temperature range for the cyanate ester component of the curable PSA is from approximately 20°C to 300°C with a preferred range of
15 30-200°C and a most preferred range of 40-150°C. Lower cure temperatures generally will require longer cure times than higher temperatures and cure times may range from a few seconds to several days. For example, in bonding flex circuitry a bond time of 5-50
20 seconds at 150-200°C is desirable while in bonding automotive body panels to a frame a bond time of 30 minutes at 120°C is acceptable.

Compositions of the invention can be exposed to actinic radiation through a mask to produce patterned
25 coatings, to photocure one or both components of the composition. For use as a patterned adhesive, it is desirable to photocure only one component to generate the image; the second component is subsequently cured, preferably thermally, after the adhesive-coated
30 substrate is placed in contact with a second workpiece. In this manner, adhesive may be applied only on the areas of a substrate that are to be bonded, avoiding possible damage due to poorly positioned adhesive.

35 For use as a photoresist, solder mask, printing plate, protective coating or printed circuit pattern,

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e.g., where non-PSA coatings are desired, it is desirable that both components be photoactivatable. Exposure through a photomask cures the ethylenically unsaturated monomer while simultaneously activating 5 the cyanate ester catalyst in the exposed areas. The cyanate is then cured by oven heating at temperatures between 50 and 250°C, preferably 80 - 150°C. Or, the coated substrate may be irradiated at an elevated 10 temperature (as above) through a mask, whereupon cure of both components will occur simultaneously.

In all of the above cases, the imaged coating is developed by washing with a suitable solvent, such as methanol, ethanol, isopropanol, methyl ethyl ketone, cyclohexanone, toluene, tetrahydrofuran, or ethyl 15 acetate, or mixtures thereof. The developed coating can be used as such or may be post-cured by heating to temperatures generally higher than those required to fix the image, and may range from 50 - 300°C, preferably 100 - 200°C.

20 Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this 25 invention.

In the examples Me = methyl, Ph = phenyl, Cp = cyclopentadienyl, Mes = mesitylene.

All syrups unless otherwise stated were made by adding 0.05% KB-1 by wt. to the monomer and exposing 30 to 350 nm UV light. The syrup making device allows for constant stirring and rotation along with a N₂ purge bubbling through the mixture. The UV light is placed 20.3 cm (8 inches) from the center axis of the jar. Tests have shown that the amount of energy from 35 the lights at this distance is 67 mJ/cm²min. The

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syrups have Brookfield viscosities from 1000 to 3000 cps.

Examples

- 5 Example 1: One part Quatrex-7187™ cyanate ester resin (Dow Chemical) was mixed with one part iso-bornyl acrylate (Sartomer Co.) syrup and one part iso-octyl acrylate (Sartomer Co.) to give stock resin A. Cyanate ester catalysts and free radical catalysts
- 10 were added to aliquots of stock resin A as indicated in TABLE I, below. The aliquots were Meyer bar (#28) coated, 0.025 mm thick, onto a steel plate, 152 x 51 x 0.23 mm, and the plate was cut into 51 x 9.5 mm test pieces. A second 51 x 9.5 mm steel plate was placed
- 15 on top of the test piece and the sandwich construction was clamped with two paper clips. The pieces were cured at 105°C for 2 minutes immediately followed by 10 minutes at 180°C. The resulting cured constrained layer samples were analyzed by dynamic mechanical
- 20 analysis (DMA) in the flexure mode using a Seiko Instruments DMS 110 Rheometer using a 20 mm flexible fixture. The samples were processed in the Rheometer four times by ramping from ambient temperature to 300°C at 5°/minute and quenching with cold N₂ gas.
- 25 The temperature range of the tan δ peak in the 4th run above a value of 0.06 was considered to be a measure of the effective vibration damping capacity of the sample. The data is shown in TABLE I, below.

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TABLE I
Vibration Damping Data (DMA)

Sample	Organometallic ^a or conventional cyanate catalyst	Free radical ^b catalyst	Damping range ^c begin/end	Range
1	[CpFe(CO) ₂] ₂	VR-110 ^(d)	1/277	276
2	[Cp ₂ Fe]SbF ₆	VR-160 ^(d)	198/236	38
3	[(Mes) ₂ Fe][SbF ₆] ₂	VR-110	195/243	48
4	MeCpMn(CO) ₃	VR-160	-4/151	155
5	Mn ₂ (CO) ₁₀	VR-160	26/82 206/254	56 48
6	Zn octoate*	VR-110	17/60	43

(a) 0.5%bw of the cyanate resin
 15 (b) 1.0%bw of the acrylate resin
 (c) °C, tan δ > 0.06
 (d) azobistrimethylpentane
 (e) azo-t-butane
 * comparative

20 The data show that organometallic catalysts are superior to traditional cyanate curing catalysts in providing high temperature damping materials with wide effective damping ranges from cyanate/acrylate compositions. The differences in the shapes of the tan δ curves for the samples reflects differences in the morphologies of the cured compositions and demonstrates the ability to control morphology by catalyst selection. Samples 1 and 4 have broad tan δ peaks indicative of microheterogeneously phase separated compositions. Samples 2 and 3 have sharper tan δ peaks at high temperature which indicates domination by the cyanate phase. Sample 5 shows two tan δ peaks indicative of a phase separated system. 35 Sample 6 shows a tan δ peak at low temperature indicating domination by the acrylate phase. The ability of the samples to survive several temperature

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ranges to 300°C also demonstrates their high temperature stability.

Example 2: For samples 1 to 4, cyanate ester 5 catalysts and free radical catalysts were added to aliquots of stock resin A (Example 1) as indicated in TABLE II, below.

10 Sample 5 was prepared by mixing 2 parts Quatrex 7187 cyanate ester with 1 part of IOA, prepolymerized to about 2000 cps viscosity, and 1 part of IBA, prepolymerized to about 2000 cps viscosity. This mixture was added to a catalyst solution comprised of 0.002 parts of $[\text{CpFe}(\text{CO})_2]_2$ and 0.01 parts KB-1 dissolved in 0.01 parts of methyl sulfolane.

15 The mixtures were knife coated to a thickness of 0.1 mm between two silicone treated polyester release liners and irradiated for 5 minutes under a 350 nm bulb (GE F15T8-BLB, 15 watt), and release liners were removed to give a free standing film. The film was 20 laminated between two steel plates, placed in the DMA flexure head, and analyzed as in Example 1. The data are shown in TABLE II, below.

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TABLE II
Vibration Damping Data (DMA)

5	Sample	Organometallic ^a or conventional cyanate catalyst	Free radical ^b catalyst	Damping range ^c begin/end	Range
10	1	[CpFe(CO) ₂] ^(d)	KB-1 ^(e)	25/129	104
	2	[Cp ₂ Fe]SbF ₆	KB-1	12/39	27
	3	[(Mes) ₂ Fe][SbF ₆] ₂	KB-1	24/78	54
	4	Zn octoate*	KB-1	-5/20	25
	5	[(CpFe(CO) ₂] ^(d)	KB-1	21/130	109

(a) 0.5%bw of the cyanate resin
 (b) 1.0%bw of the acrylate resin

15 (c) °C, tan δ > 0.06
 (d) 0.1 wt % of the cyanate resin
 (e) benzildimethyl ketal

* comparative

20 The data of this example show that free standing curable films may be prepared and the cyanate component does not interfere with the acrylate photocure. Photoprocessing of the organometallic samples causes the acrylate phase to dominate instead 25 of the cyanate phase. The traditional Zn octoate catalyst does not provide such morphology control through process variables.

Compared to Example 1 the data of this example show that the morphology of the compositions of this 30 invention can be controlled by the choice of processing conditions.

Example 3: Stock resin B was prepared by mixing 4 parts Dow Quatrex-7187 (cyanate ester), 3 parts isobornyl acrylate, and 1 part phenoxyethyl acrylate (Sartomer Co., Exton, PA). Cyanate ester catalysts and KB-1 photoinitiator were added to aliquots of resin B in the proportions shown in Table III. The

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aliquots were knife coated to a 0.04 mm thickness
 between silicone coated polypropylene films 0.05 mm
 thick (Toray) and irradiated for 8 minutes with two 8
 watt Sylvania blacklights (350 nm) to give free
 5 standing films. The films were analyzed by DSC
 (ramped from ambient to 225°C at 10° per minute) and
 the results are shown in TABLE III, below.

TABLE III
Differential Scanning Calorimetry

Sample	Cyanate ester catalyst (g)	KB-1(g)	Resin B (g)	DSC exotherm (°C) Onset	DSC exotherm (°C) Peak
1	[CpFe(CO) ₂] ₂ (0.025) ^e	0.051	5.00	94.5	130.5
2	[Cp(xylenes)Fe]SbF ₆ (0.027) ^e	0.048	4.99	105.4	127.4
3	[(Mes) ₂ Fe] ₂ [SbF ₆] ₂ (0.025) ^a	0.053	5.00	119.4	153.5
4	[Cp ₂ Fe]SbF ₆ (0.026) ^a	0.049	4.95	99	177.3
5	Zn naphthenate ^b (0.048)*	0.055	4.98	109.2	156.4
6	Co naphthenate ^b (0.053)*	0.048	5.00	107.6	154.3
7	Mn naphthenate ^b (0.053)*	0.048	4.98	128	179.4
8	Cu Acac ^c (0.085)*	0.051	5.02	194.2	--d--

(a) in 0.08 grams of methyl sulfolane

(b) In mineral spirits

(c) copper acetylacetone

(d) peak not observed

(e) no solvent

comparative

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The data show that organometallic catalysts are effective curatives at lower loadings than traditional cyanate ester catalysts. Additionally, 5 dispersents and co-solvents required with traditional cyanate ester catalysts are not required with the organometallic catalysts. The data also show the cyanate ester is thermosettable after acrylate photocuring and that organometallic catalysts, 10 especially $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{CpFe}(\text{arene})]^+$, are the most active catalysts.

Example 4: The films prepared in Example 3 were used to prepare the constrained layer samples of TABLE IV, 15 prepared as described in Example 2. The samples were analyzed by DMA as in Examples 1 and 2. In all cases, at least two distinct maxima were observed in the $\tan \delta$ curves which is representative of phase separation. The portion of the $\tan \delta$ curve above 20 0.045 was taken to be the vibration damping range for comparative purposes and the data are shown in TABLE IV, below.

TABLE IV
Vibration Damping Data (DMA)

Sample	Organometallic catalyst or conventional cyanate catalyst	Damping range ^a begin/end (range)	Low temp max (°C/intensity)	High temp max
1	[CpFe(CO) ₂] ₂	130/230 (100)	157/0.108	224/0.051
2	[Cp(xylenes)Fe]SbF ₆	140/240 (100)	172/0.103	226/0.059
3	[(Mes) ₂ Fe][SbF ₆] ₂	128/180 (52)	151/0.115	248/0.057
4	[Cp ₂ Fe]SbF ₆	140/190 (50) 220/240 (20)	163/0.113	232/0.052
5	Zn naphthenate*	150/210 (60)	171/0.111	275/0.035
6	Co naphthenate*	135/240 (105)	158/0.118	223/0.052
7	Mn naphthenate*	130/300 (170)	152/0.100	230/0.072 260/0.065
8	Cu Acac*	125/167 (42)	146/0.109	234/0.028

(a) °C, tan δ > 0.045
* comparative

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Compared with Example 2, the data of this example show that changing the acrylate composition can dramatically change physical properties of the cured materials even when the processing conditions are 5 essentially the same.

Example 5: The films from Example 3 were used as a film adhesive to bond 2 x 2 x 1.25 mm glass test chips (cut from a microscope slide) to a microscope 10 slide. A 10 x 10 mm piece of adhesive film (as provided in Example 3) was pre-tacked to the microscope slide and 4 test chips were simultaneously bonded to the adhesive covered area using at 180°C and 4.22 Kg/cm² for 20 seconds using a vice with 15 heated coplaner platens. The bonded chips were allowed to cool under pressure to 100°C and were then removed from the bonder. The adhesion of the chips was analyzed using a die shear tester (Semiconductor Equipment Corp. Die Shear Tester Model 6000) and the 20 data for average shear energy required to remove the chips is shown in TABLE V, below.

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TABLE V
Shear Adhesion (Glass Chip)

Sample	Cyanate ester catalyst	Shear to failure (g/mm ²)
1	[CpFe(CO) ₂] ₂	661
2	[Cp(xylenes)Fe]SbF ₆	546
3	[(Mes) ₂ Fe][SbF ₆] ₂	423
4	[Cp ₂ Fe]SbF ₆	411
5	Zn naphthenate*	554
6	Co naphthenate*	535
7	Mn naphthenate*	414
8	Cu Acac*	397

* comparative

The data of TABLE V show that the dry adhesive films and organometallic catalysts for cyanate ester curing, especially [CpFe(CO)₂]₂, gave useful adhesion in chip bonding applications. Compared to data of Example 3, the data of TABLE V correlate with the DSC exotherms of the adhesive films. The organometallic samples, especially 1 and 2, could be used in chip bonding applications at bonding temperatures well below 180°C.

Example 6: A commercially available polyvinylbutyral (Butvar™, Monsanto Chemical Company, St. Louis, MO) co-polymer, 29 mol % vinyl alcohol, was converted to an acryloyloxy derivative by condensation of isocyanatoethylene methacrylate (IEMA) with the vinyl alcohol hydroxyl groups to the extent of 60 %. Coatings of this polymer with various organometallic compounds were cast from solutions comprising 2 g polymer (20 wt % in tetrahydrofuran, THF) and 0.1 g

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of the organometallic. The coatings were spread on polyester film with a #40 Meyer Bar and oven dried (1 min at 80°C). Samples were exposed to a medium pressure Hg source in a Berkey-Ascor vacuum frame

5 through a square root of 2 step tablet (Stouffer Sensitivity Guide, Stouffer Graphic Arts Equipment Company, South Bend, IN), and immediately thereafter developed in isopropanol to reveal any negative resist image which may have been formed on the

10 support by photocuring of the polymer. The data is shown in TABLE VI, below in which the result, e.g., "solid 1" means that the coating was completely insolubilized by exposures greater than or equal to that reaching the sample through step #1 of a step

15 tablet.

TABLE VI
Acrylate Photoimaging

Sample	Catalyst	Exposure time	Result
1	MeCpMn(CO) ₃	2 min.	well defined resist; solid 1; "ghost" 2-3
2	[CpFe(CO) ₂] ₂	2 min.	no image
3	[CpW(CO) ₃] ₂	2 min.	no image
4	CpFe(CO) ₃ SnPh ₃	2 min.	no image
25	5 (C ₆ H ₅)Cr(CO) ₃	2 min.	well defined resist; solid 6, "ghost" 7
6	none	2 min.	no image

20 The data show that neutral, mononuclear organometallic complexes containing polyene ligands and carbonyl ligands (samples nos. 1 and 5) are effective photocatalysts in free radical curing.

Example 7: A solution of acrylamide (1 g., Aldrich Chemical Co.) and MeCpMn(CO)₃ (0.10 g.; Aldrich 35 Chemical Co.) in tetrahydrofuran (1 ml) was prepared

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and irradiated in a quartz cuvette for 2 min in front of a medium pressure Hg arc lamp. Absorption spectroscopy revealed a new band in the irradiated solution centered on 425 nm; no further changes were 5 observed in this irradiated solution when it was allowed to stand in the dark. A solution of similar composition, similarly irradiated, was purged with dry nitrogen and sealed to exclude air; when this deoxygenated solution was allowed to stand, sealed, 10 in the dark for an additional 96 h, the acrylamide was completely converted to insoluble polymer and the characteristic yellow color of the photoproduct had disappeared.

This Example illustrates that the photoreaction 15 generates the initiator for the subsequent air-inhibited polymerization.

Example 8: A monomer composition was prepared by mixing 5 parts Quatrex-7187 cyanate ester with 3 20 parts of an isobornyl acrylate partially polymerized syrup of 2870 cps viscosity and 2 parts of a 4000 cps viscosity partially polymerized syrup prepared from 9 parts isooctyl acrylate and 1 part tetrahydrofurfuryl acrylate monomers. The mixture was stirred and 25 heated at 100°C for 30 minutes and cooled with stirring to room temperature. One percent, by weight of the acrylate components, of (benzildimethyl ketal) KB-1 was dissolved into the mixture and the mixture was divided into two portions. In one portion, 0.5 %, by 30 weight of the cyanate component, of $[\text{CpFe}(\text{CO})_2]_2$ was dissolved. In the other portion, 0.5 %, by weight of the cyanate component, of zinc octoate (8% in mineral spirits) was dissolved. Both mixtures were coated to a 0.025 mm thickness between two 35 silicone coated polyester release liners and photocured by exposing to the light from two GE

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F15T8/BLB bulbs for 5 minutes. The liners were removed and 25 x 25 mm samples of the resulting adhesive films were laminated onto one end of several .25 x 152 x 0.30 mm steel bars. These bars were 5 placed in a 180°C oven for various lengths of time ("precure time"), removed, and allowed to cool. A third piece of 25 x 25 mm film, which had not been subjected to any heat treatment, was laminated between two steel bars which had been in the oven for 10 equal periods of time such that the adhesive portions were placed on top of one another giving overlap shear test samples with three layers of adhesive film between the steel bars. These constructions were clamped with paper clips and placed in a 180°C oven 15 for time periods ("bond times") equal to the time periods of the first heat treatment. The samples were evaluated by overlap shear at room temperature in a standard moving crosshead load frame using a separation rate of 1.27 mm/min. The results are 20 shown in TABLE VII and each entry is the average of the results for 3 individual overlap shear specimens.

25 TABLE VII
Overlap Shear Adhesion

25	Precure time (minutes at 180°C)	Bond time	Shear values (g/mm ²) for [CpFe(CO) ₂] ₂ Zn octoate
0.5	0.5	298	379
1.0	1.0	517	314
30	2.0	790	269
4.0	4.0	778	217
5.0	5.0	623	242

35

The data in TABLE VII show the compositions of this invention to be superior adhesives to those

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using conventional cyanate ester catalysts; the average of the shear values for the $[\text{CpFe}(\text{CO})_2]_2$ samples (601 g/mm^2) is more than two times greater than the average of the shear values for the Zn octoate samples (284 g/mm^2). The data also show the beneficial effect of processing induced morphology changes by the increased shear values for the $[\text{CpFe}(\text{CO})_2]_2$ samples with longer pre-cure/bond times.

10 Example 9: Samples of the two adhesive films prepared in Example 8 were aged at room temperature for 24 hours and were then used to prepare overlap shear test specimens. The film prepared with Zn octoate was no longer tacky after aging while the 15 film prepared with $[\text{CpFe}(\text{CO})_2]_2$ remained tacky. The specimens were prepared and evaluated as in Example 8 and the results are shown in TABLE VIII.

TABLE VIII Overlap Shear Adhesion			
Precure time (minutes at 180°C)	Bond time (3.0)	Shear values (g/mm^2) for	
		$[\text{CpFe}(\text{CO})_2]_2$	Zn octoate
0.5	3.0	439	351
1.0	3.0	589	338
2.0	3.0	629	306
3.0	3.0	602	255

30 The data in TABLE VIII show the adhesive films prepared with $[\text{CpFe}(\text{CO})_2]_2$ maintain their superiority over those prepared with conventional cyanate ester catalysts even after aging of the films. The loss of 35 tack with the films prepared with Zn octoate upon aging shows the superior shelf life of the adhesives

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prepared with organometallic cyanate ester catalysts.

Example 10: Adhesive film samples were prepared by ball milling cyanate ester with preformed acrylate 5 syrups, catalysts, conductive particles, and coupling agents in the amounts shown in TABLE IX. The acrylate syrups were prepared by dissolving 1 milligram of benzildimethyl ketal (KB-1) in 100 grams of the acrylate monomer in a soda-lime glass vessel, 10 purging the system with a nitrogen bubble for 20 minutes, and irradiating through the walls of the glass vessel for 5 minutes with the light from two 8 watt 350nm lamps (Sylvania F8T5/350BL) while continuing the nitrogen purge. The compositions were 15 knife coated to a 0.04 mm thickness between 0.08 mm conventional polypropylene release liners and irradiated for 10 minutes with the light from the 2 8w 350nm lamps to give the free standing adhesive films of TABLE IX.

20

TABLE IX
Formulations for Adhesive Films

Component	Film ^a					
	A	B	C	D	E	F
Dimethyl acrylamide	2.5	--	--	--	3.5	--
Phenoxyethyl acrylate	2.5	--	1.5	2.5	1.5	--
N-vinylcaprolactam	--	2.5	--	--	--	--
N-butyl acrylamide	--	2.5	--	--	--	--
N-iso-butyloxymethyl acrylamide	--	--	3.5	2.5	--	5.0
Quatrex-7187 cyanate ester	5.0	5.0	5.0	5.0	5.0	5.0
nickel particles ^b	0.5	0.5	0.5	0.5	0.5	0.5
KB-1	0.1	0.1	0.1	0.1	0.1	0.1
[CpFe(CO) ₂] ₂	0.05	0.05	0.05	0.05	0.05	0.05
2-(3,4-epoxycyclohexyl)- ethyltrimethoxysilane	0.1	0.1	0.1	0.1	0.1	0.1

(a) amount in grams

(b) Bell Pearl[™] (Kanebo, Japan), nickel on phenolic resin particles

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The data of this example show that free standing adhesive films containing a random dispersion of conductive particles can be prepared as 100% solids formulations using the compositions of the invention.

5

Example 11: Electrical resistance (4-wire) test samples were prepared by bonding flex circuitry (Au-metallized over 35 micrometer thick Cu traces on polyimide film from Minco Products Inc., Fridley, MN) 10 to indium tin oxide (ITO) glass plates (20 Ω /square sheet resistivity from Nippon Sheet Glass, Japan) with the adhesive films of Example 10. Each flex circuit contained 17 traces of 0.2 mm width with 0.4 mm center-to-center spacings. Adhesives were first 15 pretacked to the flex circuits by application of heat (100°C) and gentle pressure (rubbing by hand with a cotton tipped wooden applicator) for 2-5 seconds. The bonds were made at 2 MPa for 20 seconds using a Unitek (Monrovia, CA) Phasemaster-4 hot-bar bonder 20 with the thermode set to 300°C; these bonding conditions heated the adhesive in the bond line to 180°C. A solid blade type thermode of 1.5 mm width was used. Electrical resistance of each adhesive 25 interconnection was measured by the four-wire method using the principles described in ASTM B 539-90 such that the net resistance not due to the interconnection was minimized to approximately 150 m Ω . Measurements were made before and after 1000 hours of aging at 60°C and 95% relative humidity. 30 The results are shown in TABLE X.

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5 TABLE X
10 Interconnection Resistance

Film	Initial resistance ^a			Aged ^b resistance ^a		
	Average	Minimum	Maximum	Average	Minimum	Maximum
A	0.502	0.454	0.609	0.674	0.619	0.755
B	0.475	0.440	0.533	1.902	1.086	7.169
C	0.456	0.412	0.501	0.473	0.435	0.502
D	0.509	0.469	0.581	0.536	0.489	0.605
E	0.505	0.464	0.549	4.974	2.285	11.029
F	0.443	0.413	0.514	0.555	0.504	0.634

15 (a) ohms
 (b) 1000 hours, 65°C, 95% RH

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The data of this example show that all the adhesive films from Example 10 gave satisfactory interconnect resistance prior to thermal and humidity aging and that formulations containing N-iso-

5 butoxymethyl acrylamide showed the best performance after aging.

Example 12: Peel adhesion test (90°) samples were prepared by bonding flex circuitry to ITO glass 10 plates with the adhesive films of Example 10 using the bonding method of Example 11. A standard moving crosshead load frame was used to measure the 90° peel adhesion of the bonds with a 2.54 mm/min peel rate before and after 500 hours of aging at 60°C and 95% 15 relative humidity. The results are shown in TABLE XI and each entry is the average of 3 test specimens.

20 TABLE XI
90° Peel Adhesion Data

Film	Initial Peel ^a	Aged ^b Peel ^a
A	98.6	71.7
B	286.3	36.8
C	425.0	321.0
D	261.1	243.9
E	118.3	81.9
F	527.0	320.3

30 (a) in gm/cm, average of three specimens

(b) 500 hours, 65°C, 95% RH

The data of this example show that the adhesive films from Example 10 which do not contain dimethyl acrylamide gave satisfactory adhesion for 35 microelectronic applications prior to thermal and humidity aging and that formulations containing N-

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iso-butoxymethyl acrylamide showed the best performance after aging.

Example 13: A solution for spin coating was prepared from 155 parts by weight (pbw) methyl ethyl ketone, 5 B-30 cyanate ester (100 pbw), CN966H90™ acrylated urethane oligomer (100 pbw, from Sartomer Co.), KB-1 (1 pbw), and $\text{MeCpMn}(\text{CO})_3$ (1 pbw). This was spun at 2000 rpm onto a 102 mm diameter, 0.5 mm thick silicon 10 wafer which had been cleaned by washing with deionized water. The coated wafer was placed in a 50°C oven for 15 minutes to drive off residual solvent and give a 9 micrometer thick coating. The dried wafer was laminated with a 0.05 mm thick 15 silicone coated polyester release liner and was photoimaged through the liner in a JBA mask aligner/exposure unit (Jerry Bachur Associates, San Jose, CA) using a resolution mask. The JBA exposure unit was equipped with a collimated 500 watt mercury 20 arc ultraviolet light source. The coating was exposed for 20 seconds at a light intensity of 15 milliwatts per cm^2 or 300 millijoules per cm^2 at a wavelength of 365 nm. The resolution mask was 152 mm by 152 mm chrome-on-glass mask. The photolithography 25 pattern was a series of lines which were 121 mm long with widths ranging from 2.5 mm to 4 micrometers. The imaged wafer was then placed in a 120°C oven for 30 minutes to fix the image. The image was developed by dissolving the unexposed regions by washing with a 30 1:1 mixture of acetone and iso-propyl alcohol. The imaged wafer was examined by optical microscopy to reveal a smooth coating with few bubbles or pinholes; unexposed areas 20 micron across were completely 35 resolved (all organic matter had been removed by the developing step) and showed vertical side walls. Smaller features were visible, but were not

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completely resolved in the developing step. The imaged coating showed good adhesion to the silicon wafer. The data of this example show that the compositions of the present invention are suitable 5 for photoresist and photolithographic applications.

Example 14: Three syrups of approximately 2000 cps were prepared independently from IOA, IBA, and a 1:1 mixture of IOA and IBA. Samples for DMA were 10 prepared from each of the three syrups and of a fourth syrup of approximately 2000 cps comprising a 1:1 mixture of the independently prepolymerized IOA and IBA syrups by adding 0.5% by weight KB-1 to the syrups, pouring each of the four syrups into 50 x 6 x 15 1 mm molds, covering the molds with a conventional silicone/polyester substrate release liner and a quartz plate (approximately 5 mm thick), and exposing the molds to 350 nm light for 10 minutes to complete the polymerization. The samples were tested on a 20 Seiko Tensile DMS 200 DMA using a 2°C/min. heating rate. The cured IOA syrup showed a single Tg at -46°C, the cured IBA syrup showed a single Tg at 100°C, the cured syrup from the 1:1 mixture of IOA and IBA monomers showed a single Tg at 37°C, the 25 cured sample from the 1:1 mixture of the IOA and IBA syrups showed two distinct Tgs at 4 and 91°C. The data is shown in TABLE XII below.

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TABLE XII
Glass Transition Temperatures

	Composition ^(a)	Initiator added after partial polymerization	Glass Transition Temperatures (Tg°C)
5	1 partially polymerized IOA (syrup A)	0.5 wt percent KB-1	-46
	2 partially polymerized IBA (syrup B)	0.5 wt percent KB-1	100
	3 partially copolymerized IOA and IBA	0.5 wt percent KB-1	37
	4 combination of syrups A and B	0.5 wt percent KB-1	4 and 91

10 (a) each partially polymerized syrup was initiated by 0.05 wt percent KB-1

15 The data of Table XII show that the use of mixtures of syrups causes increased phase separation which is not obtained from the monomers alone.

20 Example 15: To 3 g cyanate ester monomer L-10 (Ciba-Geigy) and 2 g isobornyl acrylate was added 0.05 g $\text{MeCpMn}(\text{CO})_3$ (Aldrich Chemical Co., Milwaukee, WI). The resulting mixture was coated on 0.075 mm polyester film using a #40 Meyer bar. For ease of 25 handling the coating was overlaid with 0.050 mm polypropylene film. A sample of this coating was exposed through the polypropylene cover sheet for 105 sec in a Berkey-Ascor graphic arts vacuum frame. During exposure the nearly colorless coating quickly 30 became straw colored, then took on a gray cast. At the same time gas evolution from the still fluid

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cating was apparent, especially around the edges of the sample. At conclusion of the exposure, the cover sheet was removed to leave a greasy, but not readily flowing film on the polyester support.

5 The sample was subsequently heated 25 mm from the nozzle of a hot air blower (about 95°C) long enough (about 15 seconds) to discharge the color of the coating, thought to be due to formation of complexes intermediate in the curing reaction, and to anneal
10 out the bubble pattern resulting from gas evolution during irradiation. The resulting coating was uniform and non-flowing, though slightly tacky. Unlike the coating obtained on UV treatment alone, it
15 was not removed from the support by ethanol sprayed from a wash bottle.

Similar heat treatment of coatings produced as above but with 45 sec and 5 min irradiation times yielded like results. Final coatings, however, were progressively harder, e.g., more resistant to
20 fingerprinting, with increasing UV exposure.

These results show that neutral, mononuclear organometallic complexes containing polyene and carbonyl ligands are useful as the sole catalyst in curing cyanate ester-ethylenically unsaturated
25 monomer compositions.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that
30 this invention is not to be unduly limited to the illustrative embodiments set forth herein.

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CLAIMS:

1. A composition of matter comprising a curable mixture comprising 1 to 99 weight percent of a first monomer and a curing agent therefor, the first monomer being one of 1) at least one ethylenically unsaturated monomer or 2) at least one cyanate ester monomer, and 99 to 1 weight percent of a second monomer and a curing agent therefor, the second monomer being the member of 1) or 2) that is not selected as the first monomer, wherein the curative for the cyanate ester is a transition metal-containing organometallic compound curing agent and the curative for the ethylenically unsaturated monomer is a free-radical generating curing agent or a transition metal-containing organometallic compound, said composition being capable of providing an interpenetrating network comprising a semi-phase separated morphology.
2. The composition according to claim 1 wherein said cyanate ester monomer has the formula $Q(OCN)_p$ wherein Q comprises at least one of 1) an aromatic hydrocarbon di-, tri-, or tetra-radical containing from 5 to 30 carbon atoms, wherein 1) optionally comprises at least one of (a) one to five aliphatic or polycyclic aliphatic divalent hydrocarbon groups containing 7 to 20 carbon atoms and (b) zero to 10 heteroatoms, and 2) divalent fluorocarbon group having 3 to 12,500 carbon atoms and 5 to 25,000 fluorine atoms, and p is an integer in the range of 2 to 7.
3. The composition according to claims 1 or 2 wherein said organometallic compound has the formula $[L^1L^2L^3M]^{+e} X_f$

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wherein

5 L^1 represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different selected from acyclic and cyclic unsaturated compounds and groups and carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing 2 to 24 pi-electrons to the valence shell of M ;

10 L^2 represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sigma-electrons that can be selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M ;

15 L^3 represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each M ;

20 M represents 1 to 6 of the same or different metal atoms selected from the elements of Periodic Groups IVB, VB, VIB, VIIIB, and VIII (commonly referred to as transition metals);

25 e is an integer having a value of 0, 1 or 2, such that the organometallic portion of the molecule is neutral, cationic or dicationic; each X is selected from the group consisting of organic sulfonates, halogenated metals or metalloids, and alkylated or arylated metal or metalloid; and p-toluenesulfonate, p-chlorobenzenesulfonate, BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , $FeCl_4^-$, $SnCl_5^-$, SbF_5^- , AlF_6^- , $GaCl_4^-$, InF_4^- , TiF_6^- , $CH_3SO_3^-$, $B(C_6H_5)_4^-$, $C_6H_5SO_3^-$, $CF_3SO_3^-$, SbF_5OH^- , and $SbCl_6^-$;

30 f is an integer of 0, 1 or 2, the number of anions required to balance the charge e on the organometallic portion; with the proviso that the organometallic compound contains at least one transition metal-carbon bond; and

35 with the proviso that L^1 , L^2 , L^3 , M , e , X , and f are chosen so as to achieve a stable configuration.

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4. The composition according to any of claims 1 to 3 which is a curable adhesive or a photoresist.

5. The polymerized composition according to any of 5 claims 1 to 4.

6. The polymerized composition according to claim 5 which provides a vibration damping constrained layer construction comprising a laminate of one or more stiff 10 substrates and one or more polymeric mixtures.

7. The composition according to any of claims 1 to 5 wherein at least one of said ethylenically unsaturated monomers is polymerized prior to 15 polymerization of said at least one cyanate ester monomer to provide an electronic adhesive, or a layer on a flexible backing to provide a pressure sensitive tape or a transfer tape.

20 8. A process for providing a mixture of polymerized cyanate ester monomer and polymerized ethylenically unsaturated monomer comprising the steps of

25 a) providing a polymerizable admixture according to claims 1 to 4, said mixture optionally further comprising at least one bireactive crosslinking monomer, and

30 b) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization, said curing agents being activated by energy in a simultaneous manner or in a sequential manner in any order.

35 9. The process according to claim 8 wherein said polymerization is controlled by at least one of rate of polymerization and diffusion of each component monomer

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to provide at least one of a phase separated or a phase mixed morphology.

10. A method comprising the steps:

5 a) providing at least two polymerizable mixtures, each comprising at least one ethylenically unsaturated monomers and a free-radical generating agent,

10 b) independently partially prepolymerizing each of said ethylenically unsaturated monomers to provide at least two partially prepolymerized syrups, and

15 c) combining said partially prepolymerized syrups and completing polymerization of said mixture; wherein said polymerizable mixture optionally further comprises at least one cyanate ester monomer and as curative a transition metal-containing organometallic compound.

20 11. The method according to claim 10 wherein said transition metal-containing organometallic compound has the formula $[L^1L^2L^3M]^{+e}X_f$ as defined in claim 3.

25 12. The polymerized composition prepared according to the method of claims 10 or 11.

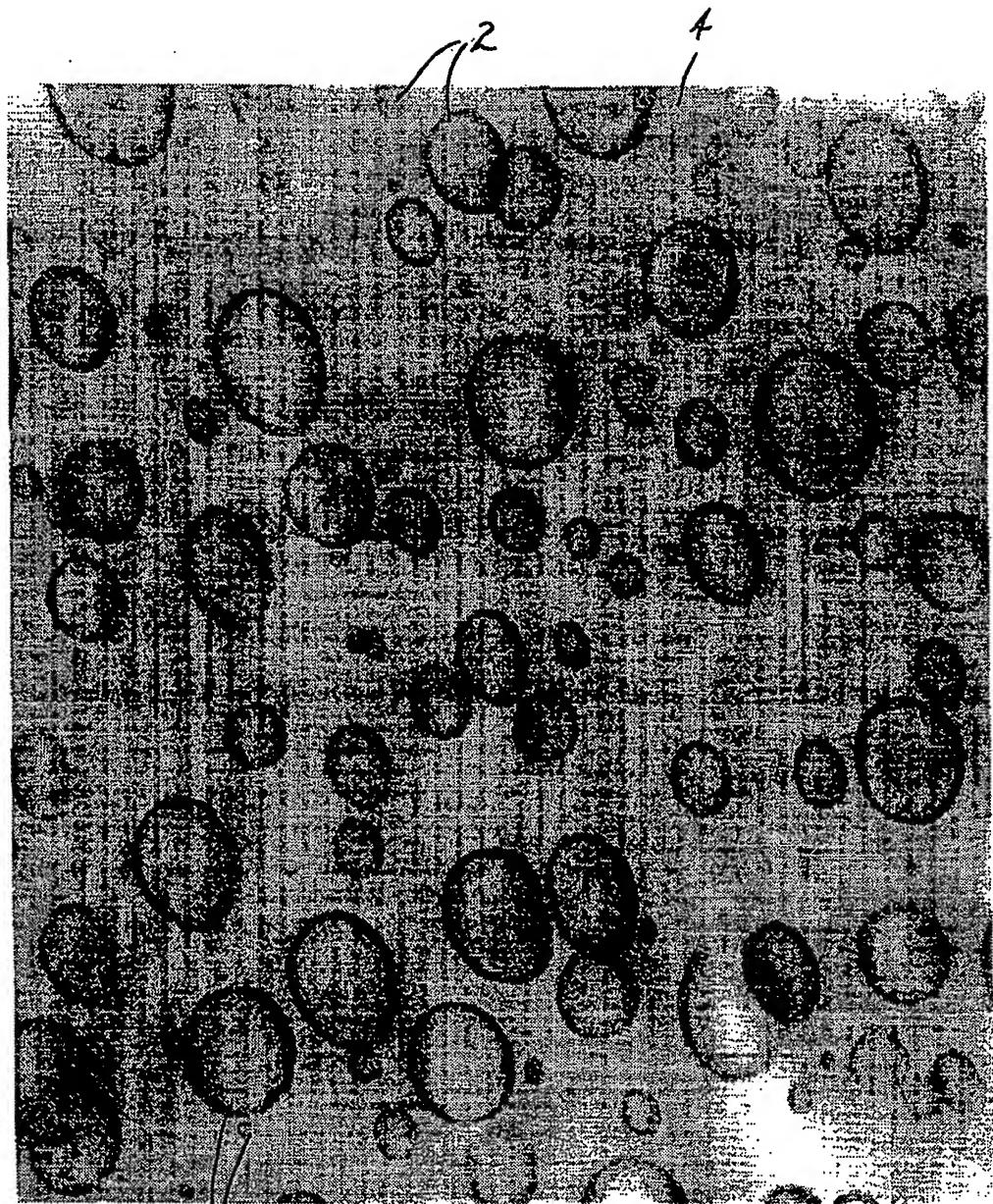


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/05240A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08G73/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,31 14 250 (MITSUBISHI GAS CHEMICAL COMPANY, LIMITED) 4 March 1982 & US,A,4 383 903 (AYANO ET AL.) cited in the application see claims 1-4 ---	1-12
A	EP,A,0 306 161 (MINNESOTA MINING AND MANUFACTURING COMPANY) 8 March 1989 see claims 1-12 ---	1-12
A	US,A,5 143 785 (PUJOL ET AL.) 1 September 1992 cited in the application see claims 1,14,28 -----	1-12

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 94/05240

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